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By Geo. K. Burgess.

Recently[1] Dr. Waidner and the author suggested two radiation methods for the determination of high melting points of substances in minute quantities. The first depends on the total radiation from a surface as measured in terms of some instrument making use of the Stefan-Bolzmann law. The second method is based on the measurement of the intensity of a particular monochromatic radiation from platinum or other substance; that is, it makes use of an instrument based on Wien's equation.[2]

Some preliminary measurements made at that time by the second method on the metals of the iron group showed it to possess considerable accuracy and to be particularly applicable to the easily oxidized elements if the melts were obtained in an atmosphere of pure hydrogen. It was also demonstrated that a compound of one of the refractory elements, which could be reduced to the metal by hydrogen, might serve as material for determining the melting point of the pure metal.

The present paper is an account of the application of this second method to the determination of the melting points in hydrogen of the members of the iron group, using, for the measurement of temperature a Holborn-Kurlbaum optical pyrometer, and the data on the monochromatic radiation from platinum published in this Bulletin.[3]

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[1] Waidner and Burgess: On the Determination of Melting Points by Radiation Method, Phys. Rev., 22, p. 359; 1906.

[2] A discussion of the laws of radiation will be found in this Bulletin, 1, p. 189; 1905.

[3] Waidner and Burgess, this Bulletin, 8, p. 1; 1907.

Experimental Method.—The arrangement of the apparatus is shown in Fig. 1, and is as follows: Within the blackened brass cylinder C is a strip of pure platinum P, about 6 cm long, 4 mm wide, and 0.02 mm thick. This platinum strip is heated electrically to any desired temperature, and by means of a rheostat, which has a fine adjustment, very delicate control of the temperature of P is obtained. The cylinder C is connected to an electrolytic hydrogen generator in series with an alkaline pyrogallate solution and a dry-
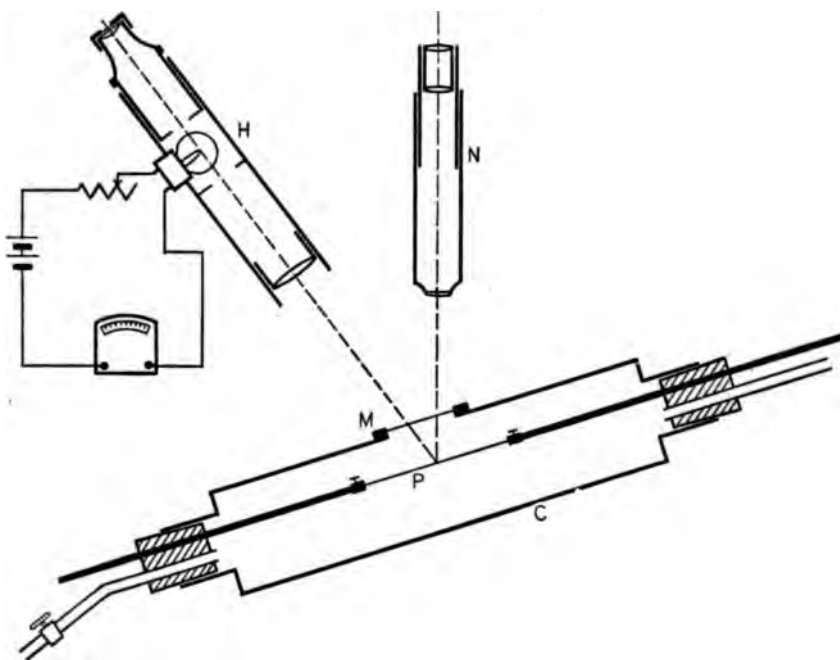
Fig. 1.

ing tube of calcium chloride. At M is a removable window of thin mica, giving access to the cylinder and permitting observation of P both with the microscope N and the optical pyrometer H.

To take an observation of a melting point, a minute quantity of a metal or its oxide, usually about 0.001 mg in the form of powder, is placed at the center of the platinum strip P, the window M screwed down, the cylinder closed and filled with hydrogen, and then the electric circuit is made through P. One observer watches the metallic speck or dust through the microscope and gradually

increases the current until the melting point is reached, while, simultaneously, another observer reads this temperature with the pyrometer.   Only one melt is taken on a given platinum strip.

Temperature Scale.—The Holborn-Kurlbaum pyrometer was calibrated by sighting upon an improved form of the electrically heated experimental black-body due to Lummer and Kurlbaum, the temperature of which was given by the electromotive forces of two platinum, platinum-rhodium thermoelements as measured on a potentiometer.   The temperature scale of the thermoelements was obtained by assuming the following melting points: $Zn = 419°.0$ C, $Sb = 630°.5$, $Cu = 1084°.0$, all these metals being of "Kahlbaum" purity.   As an upper fixed point, the melting point of platinum was taken as $1753°$ C, determined from measurements with the optical pyrometer.   In the optical pyrometer two lamps were used which gave practically identical values for every temperature observed.   As the establishment of the high temperature scale of the Bureau of Standards is treated at length elsewhere[4] in this Bulletin, further discussion of this scale need not be given here.

The indications of the optical pyrometer, when sighted upon platinum through a mica window, are subject to two corrections, one for the reflection and absorption of the mica, the other for the selective emission of the platinum for the light used—in this case, red light $\lambda = 0.66\mu$.   The former correction, which is about $15°$, is easily determined and checked between measurements of the melting points by taking observations of the platinum brightness at a definite temperature both with and without the mica interposed, with a second mica strip always in place to prevent air currents.

The correction for the selective emission of platinum is discussed in the paper above cited.   The magnitude of this correction varies from 110 to $160°$ C and is known to at least $10°$ within the temperature range here used.

Sources of the Materials.—Chemically pure elements are difficult to get, and it is desirable to use products from different sources and of known analyses.   These experiments were greatly facilitated by the willingness of scientists possessing very pure samples to put them at our disposal.

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[4] Waidner and Burgess, this Bulletin, **3**, p. 1; 1907.

M. Copaux of Paris, who has recently[6] completed a most comprehensive study of the properties of cobalt and nickel, and produced these metals containing less than 1/2000 part impurities, furnished samples of these elements. Dr. H. Goldschmidt of Essen Ruhr, Germany, sent pieces of his pure aluminothermic metals, namely, chromium and manganese, all of an average purity of 98 to 99 per cent; and Prof. C. F. Burgess of the University of Wisconsin supplied samples of his pure electrolytic iron. The other samples were from Kahlbaum and of "Kahlbaum" grade except as otherwise noted.

IRON.

Iron from two sources was used, "Kahlbaum" iron in the torm of powder, and electrolytic iron in lumps, from Prof. C. F. Burgess, from which particles weighing slightly more than 0.001 mg were chipped. This electrolytic iron had the following composition, as determined from an analysis of a similar sample by Mr. A. A. Blair, of Wisconsin:

Sulphur,	none.	Manganese,	none.
Silicon,	0.013 per cent.	Carbon,	0.012.
Phosphorus,	0.004.	Hydrogen,	0.072.

Iron as it approaches the melting point becomes plastic, so that the actual temperature of melting is not sharply defined, there being a considerable transition region.

The very considerable variation in the separate melts appears to be due mainly to the influence of size and shape of the particles on the viscosity and surface tension; also lack of homogeneity in chemical constitution of such minute samples may play some rôle, as well as variations in the temperature of adjacent areas of the platinum strip. That the electrolytic iron melts at a slightly higher temperature seems probable. Any impurity likely to be formed in iron will lower its melting or freezing point; but the total impurities in the electrolytic iron here used will not cause a lowering as great as 5° C.

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[6] H. Copaux, Recherches experimentales sur le Cobalt et sur le Nickel, Ann. Chem. et Phys., **6**, p. 508; 1905.

The corrected values found for all the separate melts are given in Table I.

TABLE I. Melting Point of Iron.

C. F. Burgess Electrolytic.	"Kahlbaum" Powder.
1493°	1509°
1519	1494
1518	1512
1512	1483
1512	1507
1514	1491
1489	——
1508	Mean . . . 1499
1508	
1494	

Mean . . . 1507

Among previous determinations of the melting point of iron have been the following:

> 1600° Roberts Austen, 1899.
> 1575° Le Chatelier, 1901.
> 1550° Osmond.
> 1555° (1490°) Tammann, 1904.

The value given by Tammann,[6] 1555°, is that, assuming the nickel point to be 1484°, as determined by Holborn and Wien.[7] Tammann's value as obtained by extrapolation of his own thermocouple calibration from the gold point (= 1064°) would be about 1490?

COBALT.

Three kinds of cobalt were used: chips from M. Copaux's sample, "Kahlbaum" cobalt, and the metal obtained from Kahlbaum's nickel-free cobalt-carbonate transformed to cobalt-oxide by heating in air, and reduced to metallic cobalt by hydrogen, in place on the platinum strip on which the melt was taken.

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[6] Guertler and Tammann, Zs. Anorg. Chem., **45**, p. 205; 1905.
[7] Holborn and Wien, Wied. Ann., **56**, p. 360; 1895.

In great contrast to iron, cobalt possesses a very sharp melting point, and the resulting precision is correspondingly increased, showing that the greater deviations in the measurements on iron are not due to the fault of the method nor to its lack of sensitiveness.

TABLE II.   Melting Point of Cobalt.

Co from CoCo$_3$ (Kahlbaum Ni-frei).	"Kahlbaum" Powder.	Copaux pieces from crucible melt.
1456°	1470°	1457°
1472	1466	1468
1467	1468	1463
1468	1466	1466
1453	1459	1462
1470	1461	
Mean . . . 1464	Mean. . . 1465	Mean . . 1463

Copaux himself gets 1530° for the cobalt point by interpolation between the gold and platinum points, assuming the latter to be 1780? Recent measurements[8] of the platinum point show 1780° to be high by about 70° on the thermocouple scale, or by about 30° on the optical scale, as usually defined in terms of Wien's law. Holborn and Valentiner,[9] however, have recently obtained 1789° for the melting point of platinum, using Wien's equation, the constants of which were newly determined by comparison with the indications of a gas thermometer up to 1600? Guertler and Tammann get 1505° for cobalt on the Holborn and Wien scale, or reduced, as explained in the case of iron, their value for cobalt would be about 1455° on the thermoelectric scale.

Nickel is usually present in cobalt to at least 2 per cent, causing a proportional lowering of the freezing point[10] of less than 1° C. Iron, even if present in considerable quantities, has a negligible effect on the cobalt melting point. Cobalt is less oxidized in the air at high temperatures than are the other elements of the iron group, and

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[8] Harker, Chem. News, **91**, p. 62; 1905. Holborn and Henning, Sitzber. Berlin Akad., **12**, p. 311; 1905. Nernst, Berichte Deut. Phys. Ges., **4**, p. 48; 1906. Waidner and Burgess, l. c.

[9] Holborn and Valentiner, Ann. d. Physik, **22**, p. 1; 1907.

[10] Guertler and Tammann, Zs. Anorg. Chem., **42**, p. 353; 1904.

cobalt oxide is only slightly soluble in the metal.[11]   These properties, taken together with its very sharp melting point, the insignificant effect of its usual impurities on this temperature, and its relative cheapness as compared with the platinum metals, make cobalt, even of a commercial purity, a desirable metal to use for a fixed point in pyrometric measurements.

NICKEL.

The melting point of nickel was determined with the pure metallic nickel of M. Copaux and with Kahlbaum's cobalt-free nickel oxide reduced by hydrogen on the platinum strip.   The melting point is about as well defined as that of cobalt.

TABLE III.   Melting Point of Nickel.

Pressed Nickel. Copaux.	Ni from the oxide. Kahlbaum.
$1434°$	$1433°$
1435	1434
1434	1439
1436	1434
1436	
Mean . . . 1435	Mean . . . 1435

The preliminary measurements of Dr. Waidner and the author showed that "Kahlbaum" nickel also gave the same value as the above.

The following thermoelectric determinations of the nickel point may be noted:

$1420°$ Le Chatelier, 1887.
$1484°$ Holborn and Wien, 1895.
$1427°$ Harker, 1905.
($1425–1430°$) Tammann, 1905.
$1470°$ Copaux, 1905.

The measurements of Copaux and of Holborn and Wien are subject to the same corrections as discussed under cobalt.   Le Chatelier's determination is based on a too low value of the gold point.   Tam-

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[11] Copaux, l. c.

mann's value is that deduced from his own observations as in the case of cobalt and iron. According to the measurements of Waidner and Burgess (1. c.) the optical is 8° higher than the usual thermoelectric scale at 1427°, so that the nickel freezing point, as determined by Harker using thermocouples, is in exact agreement with the above optical determination.

The presence of cobalt in nickel as impurity will raise the melting point,[11] while iron as an impurity in nickel will lower its melting point.

CHROMIUM.

Crystallized chromium from Kahlbaum was used and also Dr. Goldschmidt's aluminothermic chromium of 98–99 per cent purity and carbon free. As Table IV shows, it is about as difficult with chromium as with iron to get a sharp melt. Possibly the greater impurity of the crystallized chromium increases this effect for that sample.

TABLE IV.   Melting Point of Chromium.

Chromium crys. Kahlbaum.	Cr. 98–99 per cent Goldschmidt.
1501°	1497°
1472	1483
1480	1486
1505	1484
1475	1494
Mean . . . 1487	Mean . . . 1489

A thermoelectric determination of the chromium melting point has been made by Lewis,[12] using 99 per cent chromium obtained by the Goldschmidt process. The melt was made in a lime crucible in an oxy-coal-gas flame; two melts gave 1510° and 1520°.

MANGANESE.

Two samples of manganese were used: " Kahlbaum " manganese, and a sample from Dr. Goldschmidt, 98 per cent manganese, carbon free and technically iron free. The manganese point, although

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[11] Tammann, 1. c.

[12] E. A. Lewis, Chem. News, **86**, p. 13; 1902.